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INTERNATIONAL APPLICATION PUBLISHED UNDER THE PATENT COOPERATION TREATY (PCT)

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(21) International Application Number: PCT/SE93/00317 (22) International Filing Date: 13 April 1993 (13.04.93) (30) Priority data: 9201151-9 10 April 1992 (10.04.92) SE (71) Applicant (for all designated States except US): BOFORS EXPLOSIVES AB [SE/SE]; S-691 86 Karlskoga (SE). (72) Inventors; and (75) Inventors/Applicants (for US only) : CALSSON, Staffan [SE/SE]; Yttre Lötsvängen 30, S-691 35 Karlskoga (SE). SCHMID, Hermann [SE/SE]; Västra Rävåsgatan 2, S- 691 35 Karlskoga (SE).		(74) Common Representative: FALK, Bengt; Bofors AB, Patent and Trademarks, S-691 80 Karlskoga (SE). (81) Designated States: JP, US, European patent (AT, BE, CH, DE, DK, ES, FR, GB, GR, IE, IT, LU, MC, NL, PT, SE). Published <i>With international search report.</i> <i>In English translation (filed in Swedish).</i>
(54) Title: METHODS FOR PROVIDING EXPLOSIVES WITH EXOTHERMIC REACTING METAL ADDITIONS (57) Abstract The present invention relates to a method of producing explosive compositions including mechanical alloys whose components, on their detonation, give additional energy in the form of exothermic alloy reactions. The present invention also includes explosive compositions produced in accordance therewith.		

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METHODS FOR PROVIDING EXPLOSIVES WITH EXOTHERMIC REACTING METAL ADDITIONS.

TECHNICAL FIELD

The present invention relates to a novel field of use for certain so-called mechanical alloys as defined below, namely as additional energy in explosives of the most varying types. Thus, the present invention is applicable to both propellants for missile and artillery purposes and to all types of explosives and pyrotechnical charges. One precondition for this novel field of use for the so-called mechanical alloys under consideration here is that these consist of components which react exothermically with one another when they, by an intermetallic alloy reaction, together form a fusible alloy.

BACKGROUND ART

The term mechanical alloys is here taken to signify a less well-known group of metallurgical compositions which share a common method of production and general configuration. In purely general terms, the mechanical alloys may be seen as fine-grained solid dispersions produced by grinding or milling together of two or more already initially relatively fine-grained metallic materials, carbon being equivalent to a metal in this context. The grinding or milling may take place in a ball mill, a batch mill or the like and be carried out as high or low energy grinding. The grinding or milling together of the components included may further take place applying any optional proportions, without due consideration to those proportions in which the components included would normally form fusible alloys. However, one precondition for a mechanical alloy to be formed is that at least one of the components included therein is a ductile metal, by which is taken to signify a metal which is pliable in its normal state. By way of example of ductile metals, mention might be made of aluminium, titanium and nickel.

Even though the expression mechanical alloys designates a product which is ground or milled together and consists of two or more metals, this designation is not wholly irrelevant, since at least heavy metals, i.e. metals heavier than iron, which form fusible alloys with one another are most often not dissolved in one another other than within relatively narrow temperature ranges and outside of these ranges deposit in the form of crystals which lie closely adjacent one another. Fundamentally, mechanical alloys will have the same type of microstructure as such fusible alloys, but with the difference that they are obtained in finely-divided form. In the grinding or milling together of the components

included in a mechanical alloy, the first result is a crushing of the particles included, resulting in an increasingly fine-grained product which, however, after a particle minimum begins to form agglomerates according as fine particles of the materials included begin to be baked together to form composite particles. Granted, these composite particles will initially be crushed in their turn, but if no special measures are adopted, a progressive fusion will take place between the components included in the agglomerate as the temperature in the material being ground rises to the fusion temperature of the components. As a result of this mutual fusion, there will thus be obtained a progressive material accumulation of increasingly harder and increasingly larger particles which are more difficult to crush and which also give rise to a progressive material accumulation on the inside of the grinding apparatus itself.

In the present novel field of use for certain specific mechanical alloys, it is definitely not desirable to realize any such local fusion between the particles within the mechanical alloy. On the contrary, an agglomerate formation is desirable within certain limits. The fusion must be avoided since it is the additional energy which is obtained when the components included in the mechanical alloy react exothermically with one another under the formation of a liquid-phase alloy which we wish to utilize. In order, to the greatest possible extent, to be able to make use of the novel field of use according to the present invention for the mechanical alloys under consideration here, it is thus a matter of producing these mechanical alloys with the least possible fusion between the particles included therein and comprising two or more metallic components and possibly carbon which, when they form common liquid-phase alloys react exothermically with one another. That property which we, according to the present invention, wish to utilize in the mechanical alloys is, thus, the close contact of the different components with one another, while the combustion of the explosive gives that additional heat which in turn initiates the exothermic alloy reaction between the components included in the mechanical alloy, and this alloy reaction thus in turn provides additional energy whose quantity is dependent upon the components included in the mechanical alloy. The mechanical alloys are obtained in the form of granules which may have a mean diameter of up towards a few millimetres (1-2 mm) and the particle size of the subcomponents included therein of between 1 and 5 μm .

As has already been intimated, the mechanical alloys under consideration here may not, in connection with the present invention, be fused to any great extent. In order to avoid such fusion taking place while the grinding or milling together proceeds, it is possible to add certain specific additives which form a liquid or solid material film over at least the particles of one of the materials included.

As such additives, mention might be made of certain alcohols, esters, amino fatty acids, glycols and waxes. It generally applies to these additives that they must be chemically reactive with at least one of the components included in the mechanical alloy. One good example of such an additive is stearic acid which, together with, for instance, aluminium gives aluminium stearate and, in such instance, provides an extremely good protective membrane on, for example, aluminium. It further applies to the additives that these must be compatible with the explosives included in the end product. The quantity of additive of the above-intimated type which must be added on production of the mechanical alloys employed according to the present invention varies, of course, somewhat depending upon the type of additive, but, in general terms, this quantity should probably not exceed one weight per cent calculated on all components included in the mechanical alloy. However, the quantity of ground additive must be minimized to the greatest possible extent, since its presence entails that the metal components will be separated by a thin material film which impedes the formation of the exothermic molten phase alloy.

The fusion between the particles included in the mechanical alloys can, in addition to using additives of the above-discussed type, be limited to some degree by carrying out the grinding or milling together under continuous cooling.

Another method of preventing or at least restricting the fusion between the metal particles in the mechanical alloy is to carry out the grinding or milling together in an indifferent grinding liquid such as water, glycols or possibly oils. In certain cases, the grinding or milling together may need to be carried out in a protective gas (e.g. n_2) atmosphere. The grinding liquid may subsequently be removed from the finished mechanical alloy by extraction. The employment of a grinding liquid in itself need not exclude the addition of the above-discussed grinding additives, for example in the form of stearic acid. The use of grinding liquid and/or protective gas atmosphere may be a safety requirement in the production of such mechanical alloys as readily may give rise to fire or explosions.

The present invention thus relates to a novel field of use for so-called mechanical alloys of the above-defined type, namely as additional energy in the explosives, in which they, by corresponding to specific metal additives of the type described in SE-A-9003724-3 and SE-A-9002723-5 which, on combustion of the explosive, give rise to exothermic temperature-elevating intermetallic alloy reactions.

The first of the above-mentioned patent applications describes the principles of these exothermic intermetallic alloy reactions in connection with explosives, while the second application relates to the same effects in missile and ram jet fuels.

Both of these prior art patent specifications describe how it is possible, by selection of suitable metal reactants which are admixed in the explosive on their combustion, to create exothermic intermetallic alloy reactions which give considerable additional energy to the combustion of the explosive. It is immaterial whether the combustion takes place by detonation or deflagration. In addition to the choice of metal reactants, it is disclosed in these patent specifications as a requirement that these metal reactants must be present in finely-divided form and in intimate contact with one another in the explosive. It is precisely this fine-division and intimate contact between the metal reactants included which can be obtained by utilizing mechanical alloys.

The mechanical alloys not only offer metal particles of μ size, they also provide access to metal mixtures consisting of a plurality of metal particles of this μ size which have been milled together to form granules in which the metal particles which are to react exothermically and intermetallically with one another on combustion of the explosive also lie, in principle, at atom distance from one another.

In the above-mentioned prior art patent applications, reference is made to such intermetallic alloy reactions as result in borides, aluminides, silicides, alloys including alkaline earth metals and carbides.

This latter group of carbides is particularly interesting in connection with the present invention. Granted, reference might show that a certain carbide formation is generally obtained on combustion of an explosive, utilizing the carbon included in the explosive, but with the inception of the present invention and utilization of the mechanical alloys creates entirely new possibilities in that carbon in the form of graphite or carbon black may be included as the one component in the mechanical alloy. The other component may then, for example, be aluminium. Since the mechanical alloys can be manufactured in optional proportions, the present invention makes it possible to utilize the additional energy from the exothermic aluminium - carbide formation reaction. In exact analogy with the above-mentioned prior art patent applications, it is primarily the metals titanium, borium, zirconium, nickel, manganese and aluminium (and hence also carbon) which are of interest in connection with the present invention and, in this context, with the additional condition that they are present in this instance in the form of mechanical alloys.

As examples of a number of explosives whose effect may be magnified in the manner characteristic of the present invention, mention might be made of HMX, RDX, PETN, TATB, NTO, HNS, TAGN, NIGU, guanidine nitrate, TNT and nitrocellulose.

Abbreviations generally employed in the present application and within the art:

RDC = hexogen

HMX = octogen
HNS = hexanitrostilbene
PETN = pentyl or penta erythritol tetranitrate
TATB = trinitro-amino-trinitrobenzene
5 NTO = 3-Nitro-1,2,4-Triazole-5-One
TNT = trinitrotoluene
TAGN = triamino-guanidine nitrate
NIGU = nitroguanidine

10 In addition, all binders relevant in explosive contexts of both the energetic and non-energetic type may be included.

All of the metal combinations defined in the above-mentioned prior art patent application may also be brought into consideration in connection with the present invention. In addition, carbon is also included in the present context which here may actually be seen as another
15 of the metals relevant in this context for forming mechanical alloys.

In the above-mentioned prior art patent applications, mention is also made of the utilization of carbon as a component which is exothermically reactive in this context, but in that instance the intention is to refer to the carbon chemically bonded in the explosive, which must be considered
20 as something completely different.

Metal combinations, also mentioned in the previously discussed prior art Swedish patent application may be relevant in connection with the present invention.

Alkaline earth metals

25 Barium plus antigen, vismuth or tin
Magnesium plus tin
Calcium plus aluminium
Strontium plus aluminium
Beryllium plus aluminium

30 Borides

Boron plus magnesium, carbon, silica, titanium, zirconium, chromium, molybdenum, tungsten or manganese.

Aluminides

35 Aluminium plus copper, calcium, boron, titanium or zirconium, chromium, manganese, iron, cobalt, nickel, palladium and platinum.

Carbides

Carbon plus beryllium, calcium, strontium, barium, boron, aluminium.

Silicides

40 Silica plus calcium, carbon, titanium, zirconium, hafnium, chromium, molybdenum and nickel.

It further applies according to the present invention that minor additions of substances or alloys from the lanthanide group and/or the metal hafnium may be added so as to catalyze the alloy reaction according to the present invention.

The present invention has been defined in the appended claims and will now be clarified further in association with the following, more detailed reasoning.

Intermetallic explosives (in theory and in practice)

5 By calculating the effect of admixture of intermetallic reactants in high energy explosives, these mixtures will show a poorer theoretical energy yield, since the quantity of explosive is reduced. In order to exemplify this, we can consider the RDX/Mn/Al system.

(Hexogen/Manganese/Aluminium) RDX (Hexogen) contains a total of 1360
10 kcal/kg in energy, by adding (replacing) 40% of RDX with the alloy metals manganese and aluminium, the total energy effect of the mixture will be reduced to 866 kcal/kg.

The corresponding results apply to boron and zirconium. The alloy reaction $Zr+2B$ has a total energy of 690 kcal/kg, a 40% admixture gives a
15 reduction of the system to 1092 kcal/kg.

This notwithstanding, experimental results demonstrate that the effect of explosive mixtures with elements of alloy metals of the above-mentioned type gives an increased penetrative effect on, for example, steel sheet. This fact can probably be explained in two ways:

20 In theoretical calculations, no account is taken of the time factor. The time factor for exothermic alloy reactions can give favourable effects on piercing penetration etc. I.e. in that metal combinations are present in and after the detonation zone, these will influence the temperature therein, and elevate the so-called residual effect.

25 - Metal combinations of the type Mn/Al, B/Ti (Boron/Titanium etc.) react in the detonation zone in the normal state with reactants from the explosive, i.e. form oxides and carbides. As a result, alloy reactions will largely be absent. It is, therefore, important that the metals are present in as close molecular contact as possible. By having mechanically
30 preprocessed the metals together, the precondition will be obtained for converting the alloy reaction in the detonation zone and as after reaction.

By testing these systems, the following results can be mentioned:

35 The test method has been illustrated in the accompanying drawing in which reference No. 1 is an electric bursting cap, 2 is a restriction in the form of a wooden block, 3 is a test body of the explosive mixture which is to be tested, 4 is a steel sheet and 5 is a wooden support.

In the test, test inserts (3) of a diameter of 22 mm and a length of approx. 20 mm were used. Initiation was effected with the electric
40 bursting cap (1) of the VA type. The steel sheet (4) employed had a thickness of 8 mm.

Test firing with hexal, i.e. 70% RDX and 30% Al gave no penetration in the test, but only crack formation was obtained in the sheet. While a

mixture of 50% RDX and Mn/Al mixture achieves penetration with a diameter of approx. 4 mm.

WHAT WE CLAIM AND DESIRE TO SECURE BY LETTERS PATENT IS:

1. A method, in such explosive mixtures in which the energy yield on their combustion by detonation or deflagration is increased by an intermetallic alloy reaction between reactants included in the explosive mixture in the form of two or more metal components in finely divided form and in intimate contact with each other in the explosive, the metal components giving, as end product, a boride, an aluminide, a silicide, a zirconium - nickel alloy, an alloy containing at least one alkaline earth metal or a metal carbide and in which this intermetallic alloy reaction is initiated by the explosive combustion and thereafter runs more or less parallel therewith without additional energy therefrom, but while emitting energy, **characterized in that** at least one of the metal components included is a ductile metal, i.e. it is pliable in the normal state; **and that** all of the components included in the intermetallic alloy reaction are supplied in the form of granules of a so-called mechanical alloy of these components produced by grinding or milling together.

2. The method as claimed in Claim 1, **characterized in that** all of the components included in the intermetallic alloy reaction are supplied in the form of granules of a mechanical alloy produced from these components and containing up to 2 weight per cent but preferably only up to 1 weight per cent of an additive which is chemically reactible with at least one of the components included therein and which, during production of the mechanical alloy, has prevented a local fusion between particles of the different components.

3. The method as claimed in any one of Claims 1 or 2, **characterized in that** the components included in the intermetallic alloy reaction are supplied in the form of granules of a mechanical alloy with particle sizes of up to 1 mm and in which part particles of the different components of the order of magnitude of between 1 and 10 μm are included.

4. The method as claimed in any one of Claims 1-3, **characterized in that** there is added, for the intermetallic alloy reaction, a mechanical alloy including boron and titanium (B/Ti).

5. The method as claimed in any one of Claims 1-3, **characterized in that** there is added, for the intermetallic alloy reaction, a mechanical alloy including manganese and aluminium (Mn/Al).

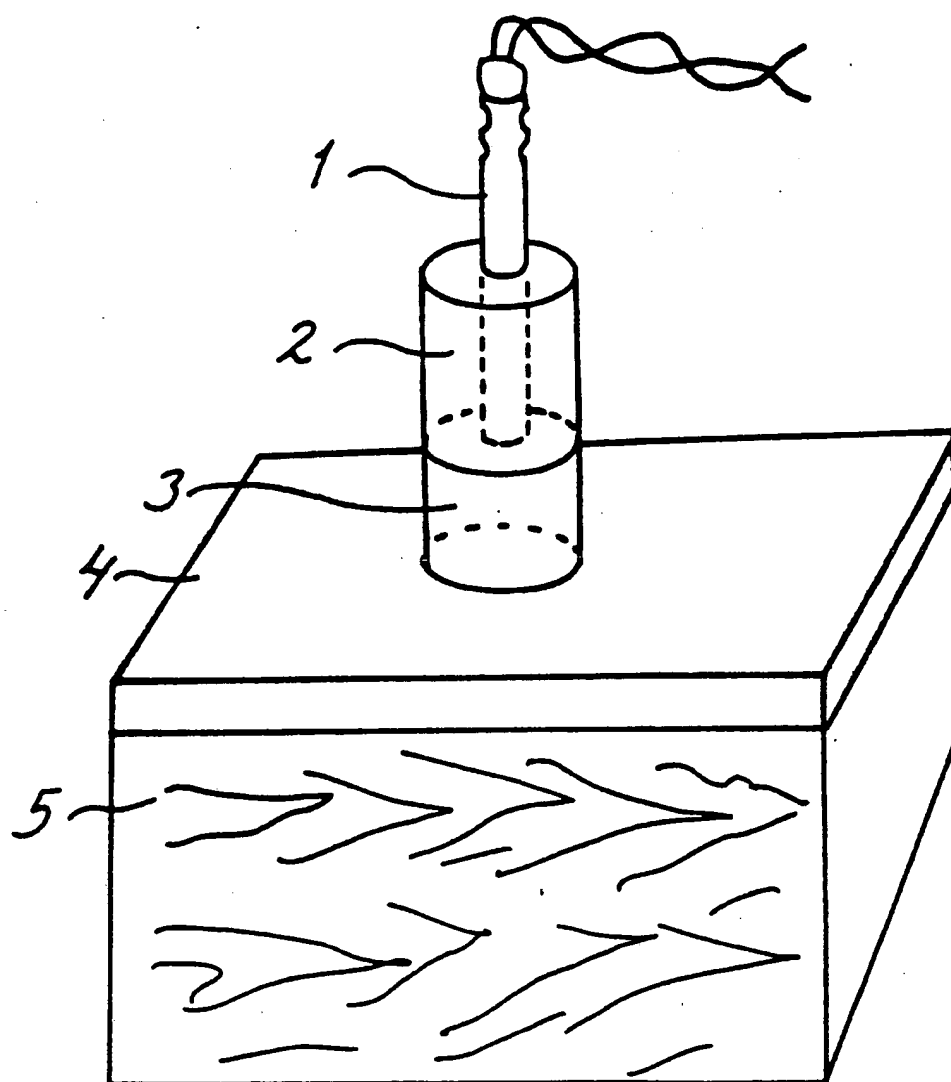
6. The method as claimed in any one of Claims 1-3, **characterized in that** the pertinent mechanical alloy is produced by dry milllion with a possible addition of grinding additive such as stearic acid in which event corresponding to at most 2% of the weight of the grinding material and preferably at most 1% thereof.

7. The method as claimed in any one of Claims 1-5, **characterized in that** the grinding is carried out as wet grinding in an inert grinding liquid.

5 8. An explosive composition produced in accordance with the method as claimed in Claims 1-7, **characterized in that** it also contains, in addition to one or more explosives, a mechanical alloy containing two or more metal components of which at least one is a ductile metal and of which one may be carbon and which, when they together form a liquid-phase alloy, react exothermically with each other.

10 9. The explosive composition as claimed in Claim 8, **characterized in that** the mechanical alloy includes boron and titanium or alternatively manganese and aluminium.

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INTERNATIONAL SEARCH REPORT

International application No.

PCT/SE 93/00317

A. CLASSIFICATION OF SUBJECT MATTER

IPC5: C06B 27/00, C06B 33/08, C06D 5/06

According to International Patent Classification (IPC) or to both national classification and IPC

B. FIELDS SEARCHED

Minimum documentation searched (classification system followed by classification symbols)

IPC5: C06B, C06D, F42B

Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched

SE,DK,FI,NO classes as above

Electronic data base consulted during the international search (name of data base and, where practicable, search terms used)

C. DOCUMENTS CONSIDERED TO BE RELEVANT

Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
A	US, A, 4331080 (MARTIN M. WEST ET AL), 25 May 1982 (25.05.82), column 2, line 61 - column 3, line 2; column 3, line 24 - line 29; column 4, line 13 - line 37, column 6, line 1 - line 5; column 6, line 47 - line 55 --	1,3,4,8,9
A	WO, A1, 9203394 (MARTIN MARIETTA CORPORATION), 5 March 1992 (05.03.92), page 7, line 5 - line 9; page 7, line 13 - line 19; page 7, line 26 - line 31, page 9, line 19 - line 22; page 10, line 29 - page 11, line 4; page 13, line 12 - line 25; figure 2 --	1,3,4,8,9

☒ Further documents are listed in the continuation of Box C.☒ See patent family annex.

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Date of the actual completion of the international search

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INTERNATIONAL SEARCH REPORT

International application No.

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C (Continuation). DOCUMENTS CONSIDERED TO BE RELEVANT		
Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
A	EP, A1, 0332745 (RHEINMETALL GMBH), 20 Sept 1989 (20.09.89), column 1, line 8 - line 9; column 1, line 20 - line 21; column 1, line 26 - line 31, column 3, line 16 - line 45 --	1,3,8
A	CH, A5, 677530 (SCHWEIZERISCHE EIDGENOSSENSCHAFT), 31 May 1991 (31.05.91), column 2, line 46 - line 49; column 3, line 1 - line 2; column 3, line 19 - line 24 --	1,3,8
A	DE, C1, 2927556 (MESSERSCHMITT-BÖLKOW-BLOHM GMBH), 9 May 1985 (09.05.85), column 3, line 10 - line 16 -----	1,8

INTERNATIONAL SEARCH REPORT

Information on patent family members

28/05/93

International application No.

PCT/SE 93/00317

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EP-A1-	0332745	20/09/89	SE-T3-	0332745	
			DE-A-	3809051	28/09/89
			DE-A-	3867229	06/02/92
			JP-A-	2078900	19/03/90
			US-A-	5028275	02/07/91
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			EP-A,B-	0369543	23/05/90
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